

Claims

1. A process for the production of hollow fibers with an external diameter from 10 nm to 100 μm , which contain at least one polymer, comprising the steps:
- (a) provision of a porous template material,
 - (b) introduction of a liquid containing at least one polymer into the pores of the template material in such a manner that the pore walls are wetted by the liquid, but the pores are not completely filled with liquid,
 - (c) solidification of the liquid and
 - (d) optionally at least partial removal of the template material.
2. The process for the production of hollow fibers of nonpolymeric materials with external diameters from 10 nm to 100 μm , comprising the steps:
- (a) provision of a porous template material,
 - (b) introduction of a liquid containing at least one polymer and at least one nonpolymeric material into the pores of the template material in such a manner that the pore walls are wetted by the liquid, but complete filling of the pores does not take place,
 - ~~(c) solidification of the liquid,~~
 - (d) selective, at least partial removal of the polymeric components,
 - (e) optionally chemical conversion of the nonpolymeric material remaining in the pores and
 - (f) optionally at least partial removal of the template material.
3. The process as claimed in claim 1 or 2, characterized in that the liquid is introduced into the pores as a melt of a polymer or a mixture of polymers, which optionally contains further additives.

4. The process as claimed in claim 3, characterized in that the melt is produced by heating to a temperature above the solidification temperature of the polymer or the polymer mixture.
5. The process as claimed in claim 4, characterized in that the melt is produced by heating to a temperature which is at least 30% above the solidification temperature of the polymer or the polymer mixture.
6. The process as claimed in one of claims 3 to 5, characterized in that the liquid is solidified by cooling of the melt.
7. The process as claimed in claim 1 or 2, characterized in that the liquid is introduced into the pores as a solution, suspension or/and emulsion of a polymer or a polymer mixture, which optionally contains further additives, in a carrier or carrier mixture.
8. The process as claimed in claim 7, characterized in that the liquid is solidified by removal of the carrier.
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9. The process as claimed in one of claims 1 to 8, characterized in that the liquid contains at least one polymer with number average molecular weights (Mn) of more than 100,000 D, preferably more than 500,000 D, especially preferably more than 1,000,000 D.
10. The process as claimed in one of claims 1 to 9, characterized in that the liquid contains at least one polymer with a molecular weight distribution with a dispersity < 2.5 , preferably < 2.0 , especially preferably < 1.10 .

11. The process as claimed in one of claims 1 to 10,
characterized in that the liquid contains at least
one partially crystalline or crystalline polymeric
component and the degree of crystallinity of the
hollow fibers is preferably adjusted by tempering
of the filled template material over a selected
time period at a selected temperature above the
glass transition temperature and below the melting
temperature of the partially crystalline or
crystalline component or/and by cooling of the
melt at a selected cooling rate.
12. The process as claimed in one of claims 1 to 11,
characterized in that phase transition processes
are induced in the material wetting the pore
walls.
13. The process as claimed in claim 12, characterized
in that the induction of segregation processes is
effected in the liquid, as a result of which
hollow fibers with regions of differing material
composition are produced.
14. The process as claimed in claim 13, characterized
in that segregation processes are induced between
~~several polymers or/and between polymers and~~
carriers.
15. The process as claimed in claim 13 or 14,
characterized in that the segregation processes
are induced by temperature changes or/and by
altering the composition of the liquid, preferably
by evaporation of a volatile component.
16. The process as claimed in one of claims 12 to 15,
characterized in that a phase separation is
induced in the liquid and a maturation of the
segregation morphology is induced by tempering at

- a selected temperature above the solidification temperature over a selected time period, and this maturation process is frozen in by means of a temperature change, preferably with a temperature change of more than 10 K/min, especially preferably more than 100 K/min.
17. The process as claimed in one of claims 13 to 16, characterized in that hollow fibers with pores in the fiber wall are produced through the segregation process.
18. The process as claimed in one of claims 1 to 17, characterized in that the liquid is introduced into a template material which is rotating, preferably at more than 500 RPM, especially preferably at more than 2,000 RPM.
19. The process as claimed in one of claims 1 to 18, characterized in that during the introduction of the liquid into the template material ultrasound acts on the liquid.
20. The process as claimed in one of claims 1 to 19, characterized in that hollow fibers are produced which contain at least two coexisting phases and ~~at least one phase is selectively removed from the~~ hollow fibers, preferably by extraction, action of radiation, chemical, biological or thermal degradation, action of ultrasound or combinations thereof.
21. The Process as claimed in one of claims 1 to 20, characterized in that a template material which contains arrays of pores parallel to one another is used.
22. The Process as claimed in at least one of claims 1 to 21, characterized in that a template material

which contains arrays of pores whose length deviates less than 15%, preferably less than 5%, especially preferably less than 1%, from the average pore length is used.

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23. The process as claimed in at least one of claims 1 to 22, characterized in that a template material which contains pores with an aspect ratio from 1 to 20,000, preferably 10 to 20,000 and especially preferably 1,000 to 20,000 is used.

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24. The process as claimed in at least one of claims 1 to 23, characterized in that a template material which contains pores with a pore diameter from 10 nm to 100 μm is used.

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25. The process as claimed in one of claims 1 to 24, characterized in that a template material which contains pores with a deviation from the average pore diameter of $< 5\%$, preferably of $< 1\%$ is used.

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26. The process as claimed in one of claims 1 to 25, characterized in that a template material which displays a pore density of more than 10^4 pores/ cm^2 , preferably more than 10^5 pores/ cm^2 , especially preferably more than 10^6 pores/ cm^2 is used.

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27. The process as claimed in one of claims 1 to 26, characterized in that a template material in which pores are arrayed in a regular manner, preferably in a hexagonal, trigonal or square lattice or in a graphite lattice, is used.

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28. The process as claimed in claim 27, characterized in that a template material which displays a lattice constant which is less than 100 nm, preferably less than 10 nm, especially preferably less than 1 nm, larger than the average pore diameter is used.

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29. The process as claimed in one of claim 1 to 28,
characterized in that a template material uses
pores selected from
- 5 (i) blind pores,
(ii) pores open at both ends,
(iii) defect pores starting from main pores, with
pore depths smaller than the distance between
adjacent main pores and pore diameters smaller
10 than the pore diameters of the main pores,
(iv) pores starting from main pores, which form a
linkage between different main pores, and
combinations thereof.
30. The process as claimed in one of claims 1 to 29,
15 characterized in that the wall thickness of the
hollow fibers is from 1 nm to 1 μ m.
31. The process as claimed in one of claim 1 to 30,
characterized in that the polymer is selected from
- 20 (i) organic polymers, such as poly(p-xylylene),
polyether imides, polyaryl ether ketones,
polysulfones, poly(phenylene sulfides),
polyacrylamides, polyimides, polyesters,
polyolefins, polystyrenes, polycarbonates,
25 polyamides, polyethers, polyphenylenes,
polysilanes, polysiloxanes,
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- polybenzimidazoles, polybenz-thiazoles,
polyoxazoles, polysulfides, polyester amides,
polyarylenevinylenes, polylactides, polyether
30 ketones, polyurethanes, polysulfones,
ormocers, polyacrylates, silicones, fully
aromatic copolyesters, poly-N-
vinylpyrrolidone, polymethacrylates such as
polyhydroxymethyl methacrylate or polymethyl
35 methacrylate, polyterephthalates such as
polyethylene terephthalate or polybutylene
terephthalate, polymethacrylonitriles,
polyacrylonitriles, polyvinyl acetates,

- neoprene, buna N, polybutadiene and halogenated polyolefins such as polyvinylidene fluoride or polytetrafluoroethene, and dendrimers,
- 5 (ii) biological polymers, such as polysaccharides, for example cellulose (modified or unmodified), alginates or polypeptides such as for example collagen,
- 10 (iii) polymers built up of two or several different repeating units, preferably in the form of block copolymers, graft copolymers or dendrimers and
- (iv) combinations of several organic polymers or/and biological polymers.
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32. The process as claimed in one of the foregoing claims, characterized in that
- (a) the liquid to be introduced into the template material contains at least one metal-containing
- 20 compound, which is preferably selected from components which
- (i) contain a metal, in particular platinum, palladium, gold, silver, nickel, rhodium, ruthenium, manganese, titanium or chromium,
- 25 another main group or transition metal or combinations of different metals,
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- ~~(ii) contain an organometallic compound or another~~
- metal-containing compound, in particular platinum, palladium, gold, silver, nickel,
- 30 rhodium, ruthenium, manganese, titanium or chromium, another main group or transition metal or combinations of different metals,
- (iii) are semiconductor materials,
- (iv) alloys of semiconductor materials and/or
- 35 (v) precursor compounds for semiconductor materials,
- (b) the organometallic compounds are optionally transformed by suitable methods, preferably chemical, biological, thermal or/and photochemical

processes or/and by the action of radiation or/and plasma.

- 5 33. The process as claimed in claim 32, characterized in that the transformation comprises the conversion of the metal-containing compound, for example an organometallic compound, into a metal or metal oxide.
- 10 34. The process as claimed in claim 32, characterized in that the transformation comprises the conversion of the metal-containing compound, for example a semiconductor precursor compound into a semiconductor compound.
- 15 35. The process as claimed in one of claims 1 to 34, characterized in that after the solidification of the liquid the template material is at least partly degraded thermally, chemically, 20 biologically, in a radiation-induced manner, photochemically, by plasma, ultrasound, microwaves or/and extraction with a solvent.
- 25 36. Porous materials, preferably polymer membranes, metal oxides, ceramics, metals or metalloids and semiconductors, especially preferably aluminum oxide or silicon, obtainable as claimed in one of claims 1 to 35, characterized in that the inner walls of their pores are at least partially coated 30 with a solid material which contains at least one polymer.
- 35 37. Porous materials, preferably polymer membranes, metal oxides, ceramics, metals or metalloids and semiconductors, especially preferably aluminum oxide or silicon, obtainable as claimed in one of claims 1 to 35, characterized in that the inner walls of their pores are coated with a

nonpolymeric material, in particular with a metal oxide and/or a metal, preferably in the form of particles with dimensions < 50 nm, especially preferably with nanoparticles of a metal oxide or/and a metal with dimensions < 3 nm.

38. Hollow fibers with an external diameter from 10 nm to 100 μm which contain at least one polymer, obtainable as claimed in one of claims 1 to 35.

39. Hollow fibers with an external diameter from 10 nm to 100 μm which contain at least one nonpolymeric material, obtainable as claimed in one of claims 2 to 35.

40. The hollow fibers as claimed in claim 38 or 39, characterized in that their diameter is constant over their whole length.

41. The hollow fibers as claimed in one of claims 38 to 40, characterized in that both fiber ends are open, one fiber end is open or both fiber ends are closed and a hollow space is enclosed.

42. The hollow fibers as claimed in one of claims 38 to 41, characterized in that their surfaces display pores, preferably with pore diameters of less than 500 nm, especially preferably of less than 100 nm, quite especially preferably of less than 10 nm.

43. The hollow fibers as claimed in one of claims 38 to 42, characterized in that they display a rough or/and structured surface.

44. The hollow fibers as claimed in one of claims 38 to 43, characterized in that their specific

surface area is $> 10 \text{ m}^2/\text{g}$, preferably $> 100 \text{ m}^2/\text{g}$, especially preferably $> 500 \text{ m}^2/\text{g}$.

- 5 45. The hollow fibers as claimed in one of claims 38 to 44, characterized in that their surface to volume ratio is $> 100 \text{ m}^2/\text{m}^3$, preferably $> 1,000 \text{ m}^2/\text{m}^3$, especially preferably $> 10,000 \text{ m}^2/\text{m}^3$.
- 10 46. The hollow fibers as claimed in one of claims 38 to 45, characterized in that their aspect ratio is ≥ 100 , preferably $\geq 1,000$, especially preferably $\geq 10,000$.
- 15 47. The hollow fibers as claimed in one of claims 38 to 46, characterized in that the inner side or/and the outer side of their surface is coated with a further material or a further material mixture, preferably by chemical gas phase deposition, physical gas phase deposition, vapor deposition, sputtering, laser ablation or wetting, currentless deposition or/and electrodeposition.
- 20 48. The hollow fibers as claimed in one of claims 38 to 47, characterized in that their inner volume is completely or partially filled with a further material or a further material mixture, preferably
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- 25 by chemical gas deposition, physical gas deposition, currentless deposition or/and electrodeposition.
- 30 49. The hollow fibers as claimed in one of claims 38 to 48, characterized in that they contain at least two different polymers in selected mixing ratios.
- 35 50. The hollow fibers as claimed in one of claims 38 to 49, characterized in that they contain regions of differing material composition, preferably

dished morphologies, especially preferably interpenetrating morphologies.

- 5 51. The hollow fibers as claimed in one of claims 38 to 50, characterized in that they contain a partly open surface, which in the direction of the fiber axis has the length of the fibers, but does not take up the whole extent of the surface.
- 10 52. The hollow fibers as claimed in one of claims 38 to 51, characterized in that they contain at least one partially crystalline or crystalline component and the degree of crystallinity is $< 40\%$, preferably $< 10\%$, especially preferably $< 5\%$.
- 15 53. The hollow fibers as claimed in one of claims 38 to 52, characterized in that they contain at least one partially crystalline or crystalline component and the degree of crystallinity is $> 40\%$, preferably $> 60\%$, especially preferably $> 85\%$.
- 20 54. Arrays of hollow fibers which contain several hollow fibers as claimed in one of claims 38 to 53.
- 25 55. The arrays of hollow fibers as claimed in claim 54, characterized in that several hollow fibers are arrayed parallel.
- 30 56. The arrays of hollow fibers as claimed in claim 55, characterized in that several hollow fibers through parallel arrangement form a freestanding membrane or are attached parallel on a substrate.
- 35 57. The arrays as claimed in one of claims 54 to 56, which are characterized by a regular array of the hollow fibers, preferably in a hexagonal, trigonal or square lattice or in a graphite lattice..

58. The arrays as claimed in one of claims 54 to 57, which have an area of more than $25 \mu\text{m}^2$, preferably of more than $500 \mu\text{m}^2$, especially preferably of more than 1 cm^2 .
59. The arrays as claimed in one of claims 54 to 58, characterized in that
- (i) the apertures of the hollow fibers are open on one side of the array,
 - 10 (ii) the apertures of the hollow fibers are open on both sides of the array or/and
 - (iii) the apertures of the hollow fibers are closed on both sides of the array.
- 15 60. The arrays as claimed in one of claims 54 to 59, characterized in that the arrays are linked to substrates on both sides.
- 20 61. The arrays as claimed in one of claims 54 to 60, characterized in that the hollow fibers are embedded in a matrix.
- 25 62. The arrays as claimed in one of claims 54 to 61, characterized in that the average spacing between the hollow fibers assumes values between double the radius of the hollow fibers and $100 \mu\text{m}$.
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- 30 63. The arrays of hollow fibers as claimed in one of claims 54 to 62 which contain hollow fibers with a deviation from the average fiber size of $< 5\%$, preferably $< 1\%$.
- 35 64. The arrays of hollow fibers as claimed in one of claims 54 to 63 which display a hollow fiber density of more than 10^5 fibers/cm^2 , preferably more than 10^6 fibers/cm^2 , especially preferably more than 10^7 fibers/cm^2 .

65. The arrays of hollow fibers as claimed in one of claims 54 to 64, characterized in that they contain deliberately introduced defect sites.
- 5 66. The arrays of hollow fibers as claimed in one of claims 54 to 65, wherein the hollow fibers are materially linked together, preferably by short fiber segments running perpendicular to the fiber axis of the hollow fibers.
- 10 67. Powders which consist of hollow fibers as claimed in one of claims 38 to 53.
- 15 68. The use of the hollow fibers as claimed in one of claims 38 to 53 for the production of nonwoven or woven textiles.
- 20 69. The use of the hollow fibers as claimed in one of claims 38 to 53 as components in medical devices, for example artificial lungs, in microelectronics as wire, cable, waveguides or capacity, in superlight construction technology, in medical separation technologies, in capillary electrophoresis, in scanning probe microscopy, in catalytic systems, in fuel cells, in batteries or
- 25 in electrochemical reactors.
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- 30 70. The use of the hollow fibers as claimed in one of claims 38 to 53 as sensor components, as microreactors, as protein storage, as drug delivery systems, as composite materials, as fillers, as mechanical reinforcement, as heat insulators, as dielectrics, as piezoelectric control elements, as interlayer dielectrics in
- 35 chip manufacture, as separation media, as storage media for gases, liquids or particle suspensions or as materials in the clothing industry.

71. The use of porous materials as claimed in claim 36 as microcell arrays in combinatorial chemistry and combinatorial materials research.
- 5 72. The use of porous materials as claimed in claim 36 as components in medical devices, for example artificial lungs, in superlight construction technology, in medical separation technologies, in capillary electrophoresis, in scanning probe
10 microscopy, in catalytic systems, in fuel cells, in batteries or in electrochemical reactors, as sensor components, as microreactors, as protein storage, as drug delivery systems, as composite materials, as fillers, as mechanical
15 reinforcement, as heat insulators, as dielectrics, as piezoelectric control elements, as interlayer dielectrics in chip manufacture, as separation media, as storage media for gases, liquids or particle suspensions, as materials in the clothing
20 industry or as functionalized surfaces with specific adhesion, tack and wetting properties.
73. The use of arrays of hollow fibers as claimed in one of claims 54 to 66 as microcell arrays in
25 combinatorial chemistry and combinatorial materials research.
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74. The use of arrays of hollow fibers as claimed in one of claims 54 to 66 as components in medical
30 devices, for example artificial lungs, in superlight construction technology, in medical separation technologies, in capillary electrophoresis, in scanning probe microscopy, in catalytic systems, in fuel cells, in batteries or
35 in electrochemical reactors, as sensor components, as microreactors, as protein storage, as drug delivery systems, as composite materials, as fillers, as mechanical reinforcement, as heat insulators, as dielectrics, as piezoelectric

control elements, as interlayer dielectrics in
chip manufacture, as separation media, as storage
media for gases, liquids or particle suspensions,
as materials in the clothing industry or as
5 functionalized surfaces with specific adhesion,
tack and wetting properties.
